

Hydrogenation of Acetic Acid on Alumina-Supported Pt-Sn Catalysts

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Abstract—Three alumina-supported Pt-Sn catalysts have been prepared by means of co-impregnation and characterized by XRD and N₂ adsorption. The influence of catalyst composition and reaction conditions on the conversion and selectivity were investigated in the hydrogenation of acetic acid in an isothermal integral fixed bed reactor. The experiments were performed on the temperature interval 468-548 K, liquid hourly space velocity (LHSV) of 0.3-0.7h⁻¹, pressures between 1.0 and 5.0Mpa. A good compromise of 0.75%Pt-1.5%Sn can act as an optimized acetic acid hydrogenation catalyst, and the conversion and selectivity can be tuned through the variation of reaction conditions.

Keywords—Acetic acid, hydrogenation, Pt-Sn catalysts, ethanol.

I. INTRODUCTION

ETHANOL is frequently used either in the production of beverages, dyes, and flavors or as fuels, such as gasohol [1], which is a mixture of ethanol and gasoline. Traditionally, there are two routes for the mass production of ethanol [2], namely fermentation of agricultural products, such as corn and sugar cane, as well as hydration of ethylene from petrochemical. However, the food crisis and the oil depletion make the aforementioned routes unattractive for the large scale production of ethanol.

A desirable synthesis method should be direct and robust and applicable on an industrial scale. Catalytic hydrogenation of acetic acid would meet these demands if suitable catalyst is

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available because theoretically acetic acid can be catalytic reduced to ethanol according to the following stoichiometry,



R. Pestman et al. have accomplished a series of experiments to explore the reactions of carboxylic acids on oxides [3-5]. Studies conducted by Willy Rachmady and M. Albert Vannice indicated that Pt supported on oxides is a promising catalyst for acetic acid hydrogenation and the most active catalyst they reported is Pt/TiO₂ with a product distribution of 50% ethanol, 30% ethyl acetate and 20% ethane[6-7].

Sn added to platinum-based catalysts has been proven to be beneficial to the activity maintenance and can modify the selectivity of catalysts. Pt-Sn/alumina catalysts have been used in soot oxidation [8], isobutane dehydrogenation [9], n-octane dehydrocyclization [10], transformation of olefins [11], crotonaldehyde hydrogenation [12] and citral hydrogenation [13].

In this study, three alumina-supported Pt-Sn catalysts with different Pt and Sn loading were prepared and tested at various operation conditions in order to maximize the selectivity of ethanol and minimize the production of byproducts.

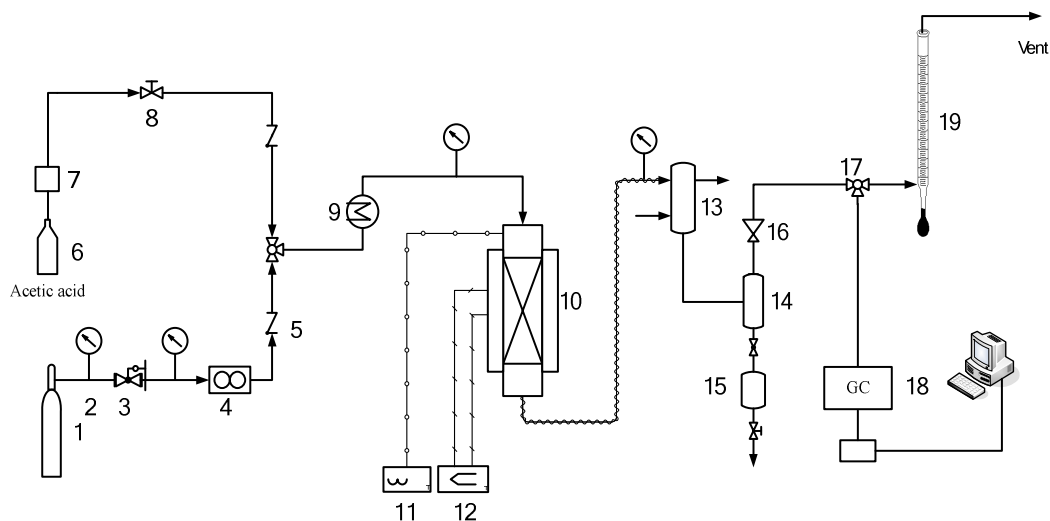
II. EXPERIMENT

A. Catalyst Preparation

Three bimetallic catalysts with different Pt, Sn content were prepared by co-impregnation. The Al₂O₃ support was ground and sieved to desired size (0.2-0.3mm) and calcined at 823K for 12h to remove organic impurities before impregnation with a solution of tin salt and platinum salt, which was prepared by dissolving certain amount of SnCl₂·4H₂O and H₂PtCl₆·6H₂O in deionized water. All the catalysts were dried in an oven at 293K overnight after aged for 12h at ambient and then calcined at static air at 823K for 12h. The catalyst was denote as aPt-bSn/Al₂O₃ where a and b represents the nominal weight percentage of each metal based on the mass of the catalyst.

B. Activity Testing

The activity and selectivity of the various catalysts prepared were tested for the hydrogenation of acetic acid in an isothermal integral fixed bed reactor (Φ14×2×650mm). Generally, the catalyst (2.8g, 4ml) was heated from ambient temperature to 623K with a ramp of 2K/min in N₂ atmosphere and then held at



1-Gas cylinder; 2-Pressure gauge; 3-Educing valve; 4-Mass flow meter; 5-Non-return valve 6-Acetic acid container; 7-Advection pump; 8-Ball valve; 9-Preheater; 10-Isothermal integral reactor; 11-Thermocouple; 12-Furnace; 13-Condenser; 14-Separator; 15-Fluid reservoir; 16-Back pressure valve; 17-Three-way valve; 18-Gas chromatograph ;19-Soap film flower

Fig. 1 Scheme of the catalyst evaluation system

623K for 2h in H₂ (0.1MPa) flow. The catalyst was cooled to the selected reaction temperature under N₂ flow and the reaction started as acetic acid was transferred into the system by H₂. The mixture of acetic acid and H₂ was preheated to maintain gas phase before entering the reactor. After passing through the condenser and the liquid-vapor separator, the effluent was sampled every 12h so as to get a steady-state performance. Composition of the tail gas was monitored on-line and the products in the liquid phase were determined off-line by a gas chromatograph Agilent 7890A. In one sampling loop, CO, CH₄, C₂H₆, N₂ and H₂ were analyzed with a molecular sieve 5A packed column (6FT×1/8IN×2.1mm), a Hayesep Q packed column (8FT× 1/8IN), and a thermal conductivity detector (TCD). In the other loop, C1-C6 oxy-compounds were analyzed with an HP-PLOT/Q capillary column (30m×0.53mm×40μm), a HP-INNOWAX (30m×0.530mm×1μm) capillary and a flame ionization detector (FID). Particularly, the concentration of acetic acid in the liquid phase was determined by titration. The setup of the employed catalyst evaluation system was depicted in Fig. 1. The carbon balance is within 5% error and the conversion, selectivity were determined with an accuracy of 5% according to the following formulas:

$$X_{HOAc} = \frac{N_{HOAc,in} - N_{HOAc,out}}{N_{HOAc,in}} \times 100\% \quad (2)$$

$$S_{EtOH} = \frac{N_{EtOH,out}}{N_{HOAc,in} - N_{HOAc,out}} \times 100\% \quad (3)$$

$$S_{EtOAc} = \frac{2N_{EtOAc}}{N_{HOAc,in} - N_{HOAc,out}} \times 100\% \quad (4)$$

C. Catalyst Characterization

The BET (Brunauer Emmett Teller) surface area, average pore size diameters, and pore size distribution were determined by means of nitrogen physisorption using a Micromeritics ASAP 2020 M automated system. All samples were degassed at 400K, 1.33Pa for 6h before adsorption.

X-ray diffraction (XRD) powder patterns of the catalysts were recorded with a Rigaku D/max 2550 diffractometer using nickel filtered Cu Kα radiation (λ=1.54056 Å) at room temperature. The X-Ray tube was operated at 40Kv ,100mA and scanned from 10°~80° at a speed of 2°/min (stepwise, 0.02) and the patterns were recorded with a 6° position sensitive detector.

III. RESULTS AND DISCUSSION

A number of reactions [14] related to acetate acid can occur on supported Pt catalysts as depicted in Fig. 2. Apart from ethanol and ethyl acetate (originated from the esterification of ethanol and acetic acid), there are also a small amount of CO, CO₂, CH₄, C₂H₆ and acetaldehyde in the products (totally less than 5%).

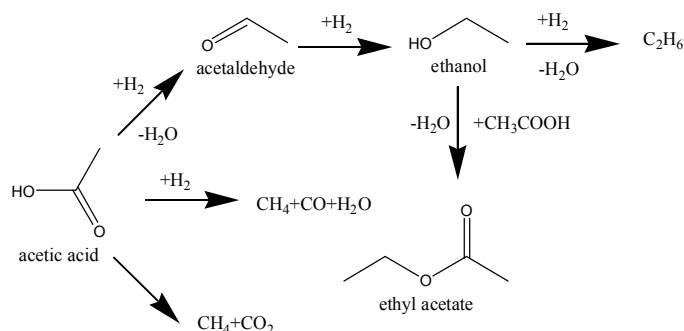


Fig. 2 Schematic diagram of stoichiometric reactions involved in the conversion of acetic acid over Pt

A. The Behavior of Various Catalysts

The performance of catalysts with different Pt, Sn loading was studied and the results are presented in Table I. The activity of the catalysts follows the order of: 0.75 Pt-1.5 Sn > 0.5 Pt-1.5 Sn > 0.5 Pt-5.0 Sn in terms of acetic acid conversion. Obviously, 0.5Pt-1.5Sn and 0.5Pt-5.0Sn shows distinct activity and selectivity. On one hand, the conversion of acetic acid increased from 67.48% to 84.54% with Sn loading declined from 5.0% to 1.5%, so was the selectivity of ethyl acetate (from 57.24 % to 32.50 %); on the other hand, the selectivity of ethanol increased from 38.94 % to 62.55 %. But Sn content was not the only conclusive factor, since the activity of 0.75Pt-1.5Sn was higher than that of 0.5Pt-1.5Sn though the variation of selectivity was not that remarkable.

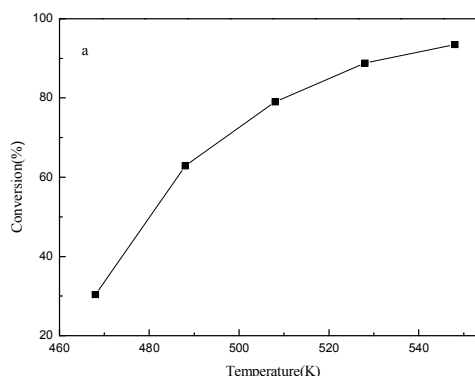
TABLE I
PERFORMANCE OF CATALYSTS WITH DIFFERENT PT, SN LOADING^A

Catalyst	Conversion %	Selectivity (mol. %)		
		ETOH	ETOAC	Others ^b
0.5Pt-5.0Sn	67.48	38.94	57.24	3.82
0.5Pt-1.5Sn	84.54	62.55	32.50	4.95
0.75Pt-1.5Sn	88.09	64.36	30.83	4.81

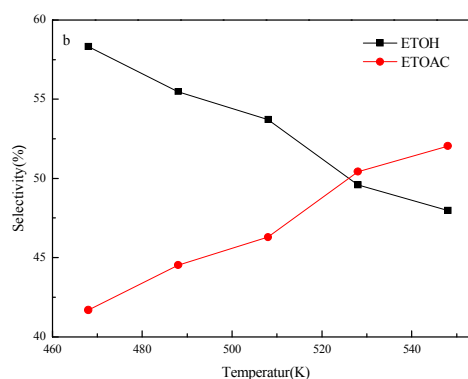
^a Reaction conditions: T=528K, P=3MPa, H₂/CH₃COOH=10, LHSV=0.3h⁻¹, ^b Others including acetaldehyde, CH₄ C₂H₆.

B. The Effect of Temperature

The impact of reaction temperature on the activity and selectivity of ethanol and ethyl acetate over 0.75Pt-1.5Sn was studied from 468 to 548K (P=5MPa, H₂/CH₃COOH=10, LHSV=0.3h⁻¹) and displayed in Fig.3. It is shown that the conversion of acetate acid increased dramatically from 30.39% to 93.42% over the range studied due to the promotion of reaction rate caused by the rise of temperature, and the higher the temperature, the less significant the acceleration of the conversion of acetate acid. The selectivity of ethanol dropped markedly as the on-going increase of temperature and the trend of selectivity of ethyl acetate is against that of ethanol.



(a) The conversion of acetic acid

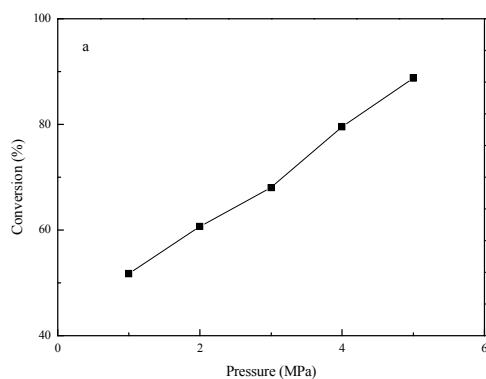


(b) The selectivity of ethanol and ethyl acetate

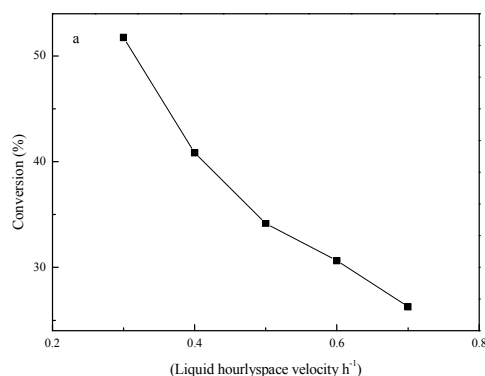
Fig. 3 The effect of temperature on the conversion and selectivity

C. The Effect of Pressure

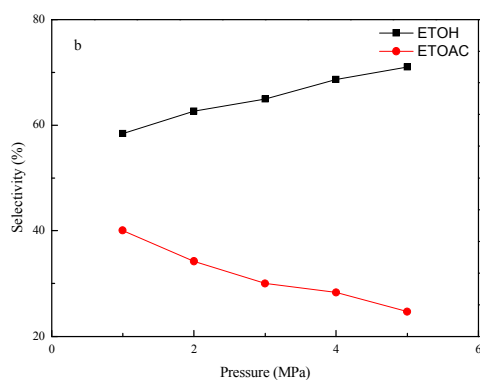
The influence of pressure has been investigated over the range of 1.0-5.0MPa when other operation conditions were fixed (T=528K, H₂/CH₃COOH=10, LHSV=0.3h⁻¹) and the results are presented in Fig. 4. The conversion of acetic acid rose along with the increase of pressure, which is result from the enhanced density of active acetate surface species and the improved collision probability of reactants and catalyst. At the same time, the selectivity of ethanol increased while that of ethyl acetate decreased, and that can be explained from the perspective of thermodynamics. There are 2 consecutive reactions in the system: the reduction of acetic acid to ethanol and the esterification of acetic acid and ethanol to ethyl acetate. The former one is a molecules reduced reaction and the number of molecules of the latter one is constant. Thus, the increase of pressure is beneficial to the production of ethanol.



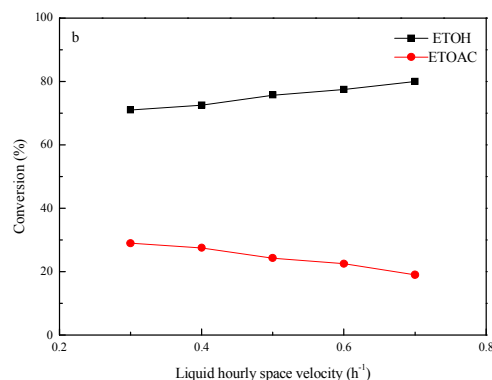
(a) The conversion of acetic acid



(a) The conversion of acetic acid



(b) The selectivity of ethanol and ethyl acetate



(b) The selectivity of ethanol and ethyl acetate

Fig. 4 The effect of pressure on the conversion and selectivity

Fig. 5 The effect of pressure on conversion and selectivity

D. The Effect of LHSV

The effects of liquid hourly space velocity (*LHSV*) on acetic acid conversion and product selectivity were evaluated ($T=428\text{K}$, $P=1\text{MPa}$, $\text{H}_2/\text{CH}_3\text{COOH}=10$) and show in Fig. 5. As *LHSV* was raised from 0.3 to 0.7h^{-1} , the conversion of acetate acid decreased from 51.75% to 30.64% due to a shortened contact time between the reactants and the surface of the catalyst result from an increase of *WHSV*. As to the selectivity, that of ethanol was improved with continued increase of *LHSV* and reached a maximum at 0.7h^{-1} while that of ethyl acetate bear a decline and dropped to 22.51% at 0.7h^{-1} .

E. Catalysts Characterization

The XRD patterns of the catalysts and the support were shown in Fig. 6. There are 3 obvious peaks located at $2\theta=38, 46$ and 67° , which can be ascribed to $\gamma\text{-Al}_2\text{O}_3$ [15]. The presence of Pt, Sn and Pt-Sn alloy phases were not detected in our samples, probably due to that the Pt and Sn are highly dispersed on the alumina support and/or that the size of the crystallite is too small to be detected by XRD detection.

The BET surface area (S_{BET}), pore volume (V_p), and average pore diameter (D_p) of the catalysts and the support are listed in Table 2. For Al_2O_3 support, the surface area is formed by the micro/meso-pores and it is capillary effect that dominates the impregnation procedure [16]. The surface area, pore volume and average pore diameter of the catalysts is lower than that of the support due to the blockage of parts of small pores caused by metal loading, and the differences among the catalysts is slight because of a low metal loading. The N_2 adsorption-desorption isotherms (Fig. 7) reveal that the catalysts and support all showed the properties of typical mesoporous materials.

TABLE II
 S_{BET} , V_p AND D_p OF THE SAMPLES

Sample	$S_{\text{BET}}(\text{m}^2\cdot\text{g}^{-1})$	$V_p(\text{cm}^3\cdot\text{g}^{-1})$	$D_p(\text{nm})$
support	313.11	0.50	6.38
0.5Pt-5.0Sn	299.85	0.44	5.54
0.5Pt-1.50Sn	305.83	0.45	5.52
0.75Pt-1.50Sn	307.35	0.45	5.52

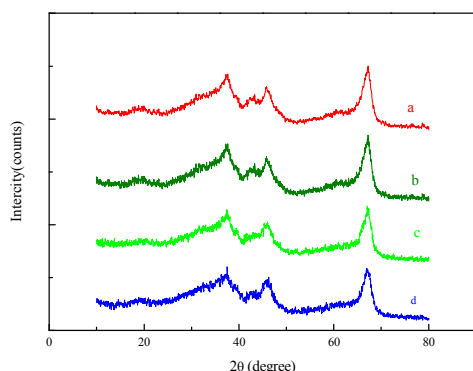


Fig. 6 XRD patterns of the samples; a-0.75Pt-1.5Sn; b-0.5Pt-1.5Sn; c-0.5Pt-5.0Sn; d-Al₂O₃

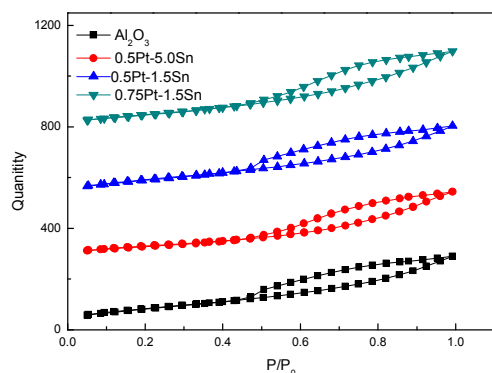


Fig. 7 N₂ adsorption-desorption isotherms of the samples

IV. CONCLUSIONS

Alumina supported Pt-Sn catalysts have been evaluated in the acetic acid hydrogenation at 528K, 3MPa, H₂/CH₃COOH=10 and LHSV=0.6h⁻¹. Among the three catalysts, 0.75Pt-1.5Sn shows the highest acetic acid conversion (88.09%) and ethanol selectivity (64.36%). The effect of reaction conditions (temperature, pressure, LHSV) on the activity of 0.75Pt-1.5Sn was studied and results show that product distribution could be achieved feasibly by adopting different temperature, pressure and LHSV. The catalysts and the support were characterized by N₂ adsorption and XRD and results show that the impregnation of Pt, Sn caused little change to the texture properties of the support.

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